

EXECUTIVE SUMMARY

Atmospheric particulate matter (PM) is of a great concern due to adverse impacts on public health, visibility degradation, and radiative forcing effects upon global climate. As source identification is a prerequisite for effective control of the levels of PM in the air, failure to definitively identify sources represents a major roadblock to improved air quality and the resulting decreases in mortality, cancer, respiratory disease, and hospital admissions. This study was motivated by a desire to improve understanding of the sources contributing to the carbon that is an important component of airborne ambient particles. More accurate source apportionment supports ARB in developing efficient control strategies. The ultimate goal of this project was to lay the ground work for future tools that might be easily implemented with archived or routinely collected samples so as to better identify sources of atmospheric particulate matter.

This study was designed to determine whether proposed sampling strategies could collect sufficient PM mass for reliable radiocarbon measurement and to evaluate whether analytical techniques could be applicable to routinely collected PM samples. A key feature of this study was application of radiocarbon measurement and source marker analyses on the same samples so that a combination of results might provide further resolution of source contributions than otherwise available. The primary distinctive feature of this study is the analysis of size-resolved and time-resolved PM samples for their radiocarbon content. The ratio of radiocarbon (^{14}C) to total carbon ($^{12}\text{C} + ^{13}\text{C} + ^{14}\text{C}$) in PM is used to estimate the percent of carbon originating from modern versus fossil sources with much greater accuracy. The carbon fraction is further differentiated by analysis for source-specific molecular markers such as alkanes and levoglucosan.

This project consisted of two phases that resulted in sample collection during two seasons, late fall (November 28-December 1; Phase I) 2007 and spring (March; Phase II) 2008. All samples were collected at a site (Del Paso Manor Elementary School) located in a residential neighborhood in Sacramento. The first phase was a pilot study intended to demonstrate and validate the proposed sample collection strategies for the differentiation of modern carbon from fossil carbon in size-fractionated PM and time-resolved bulk PM_{10} using radiocarbon measurement. PM samples were further analyzed for source-specific compounds. The sampling strategies that were validated in the first phase were duplicated for three sampling periods in the second phase. Particles resolved in 6 sizes ranging from 0.056 to 1.8 μm (aerodynamic diameter) were collected using micro-orifice uniform deposit impactor (MOUDI) samplers. To distinguish the contribution of different sources during different time periods of day (morning: 6am-11am; afternoon: 12pm-6pm; overnight: 7pm-5am), time-resolved PM_{10} samples were collected. Size-resolved PM samples were analyzed for radiocarbon and time-resolved PM_{10} samples were analyzed for radiocarbon and source-specific markers.

Carbon mass (organic carbon plus elemental carbon) of all samples (except one) collected for the present study was sufficient to measure radiocarbon content with high levels of confidence. One or two days of sampling is likely to be sufficient to collect the required amount (30 μg as carbon) of all size ranges of fine particles using two MOUDI samplers (30 mL/min) during the wintertime when ambient PM levels are high, while at least 3 or 4 days of collection was necessary during the spring and fall when ambient PM levels are low. In the case of bulk $\text{PM}_{1.8}$ (10 mL/min, 47 mm ID filter) and PM_{10} (1,130

mL/min, 8 in × 10 in filter), one day of sampling is probably sufficient to collect enough carbon during spring/fall and winter.

The radiocarbon data indicates that the contribution of non-fossil carbon sources was much greater than that of fossil carbon sources in all samples. Fossil carbon content in size-resolved PM collected in Phase I and Phase II varied from 14 to 25% and 17 to 37%, respectively, and smaller size particles had slightly greater fossil carbon fractions. Radiocarbon content indicates that the contribution of non-fossil carbon sources was higher in Phase I samples than in Phase II samples. A greater contribution of modern carbon in Phase I samples is highly likely due to residential wood combustion around the sampling site. The contribution of particles from modern carbon sources was always 7 to 16% greater in overnight samples than in morning and afternoon samples probably because of greater wood burning and lower traffic activity during the overnight period.

Among the quantified individual organic compounds, levoglucosan, which is a good chemical marker for wood burning, was the most abundant, ranging from 23.6 to 3,360 ng/m³. Levoglucosan concentrations were also much higher in Phase I samples than in Phase II samples, indicating that residential wood burning was highly likely a cause of higher non-fossil carbon fraction. When fossil carbon fractions are plotted against levoglucosan to organic carbon (Levo/OC) ratios in all samples, they showed a good negative correlation. This plot generally indicates that when the levoglucosan contribution to OC increased by 10%, the fossil carbon fraction declined by 16%. This plot demonstrates that more robust and detailed source profile can be obtained when radiocarbon and conventional source marker results are combined together.

The EC/OC ratio of the MOUDI PM_{1.8} sample collected during Phase I (0.35) was greater than those of Phase II samples (0.28 ± 0.03), indicating that the Phase I sample had a higher fraction of combustion originated particles, most likely from residential wood combustion as suggested by radiocarbon and levoglucosan data. Among the time-resolved PM₁₀ samples, the Phase I overnight sample had a much higher EC/OC ratio (0.28) than other samples (0.18 ± 0.04). This high EC/OC ratio indicates that wood combustion is likely a significant source of EC and it may not be reasonable to use EC as a diesel emission tracer in areas where wood combustion could be a confounding source of EC.

Alkane patterns in all samples, except the Phase I overnight sample, were very similar to each other. All samples showed a strong biogenic signal having carbon maximum (C_{max}) at C₂₉ and C₃₁ and a less significant input of gasoline vehicle emission. Wood combustion most significantly increased the levels of more carcinogenic PAHs such as benzo[a]pyrene. Cholesterol was not detected or was present at very low concentrations in all samples probably because particles generated from meat cooking were not significant contributors at this site or collection duration was not enough to collect measurable amounts of cholesterol.

Sample collection strategies and analytical techniques used in this study can be successfully applicable to archived and routinely collected samples if they are stored frozen (-20 °C). The results of this study also demonstrate that more robust and detailed source contribution can be obtained when radiocarbon and conventional source marker data are combined together. It is desirable to compare the source contribution results of this study with source attribution of PM samples collected at the Del Paso Manor monitoring site by the Sacramento Metropolitan Air Quality Management District.